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Highlights

- A long trianthracene molecule is used for logical operations using single metal atom contact inputs.
- Energy difference of the ground state between before and after atom contact is large enough for the NOR logic gate functioning of this molecule.

Long Starphene Single Molecule NOR Boolean Logic Gate

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Abstract

Using a low temperature scanning tunneling microscope (LT-UHV-STM), local electronic tunneling spectroscopy and differential conductance mapping are performed to investigate how by extending one phenyl more each branch of the conjugated board of a trinaphthylene starphene molecule, the corresponding longer trianthracene starphene new molecule is functioning like a NOR Boolean logic gate according to a Quantum Hamiltonian Computing (QHC) design. Here the STM tip is used to manipulate single Au atoms one at a time for contacting a trianthracene molecule. Each Au atom is acting like a classical digital input on the molecule encoding for a logical “0” when the atom is not interacting with the trianthracene input branch and for a logical “1” when interacting. The inputs are converted in quantum information inside the trianthracene molecule and the logical output status available on the output branch. QHC is demonstrated to be robust since quantum information transfer can be used on the long range along the trianthracene for the NOR logic gate to function properly as compared to the shorter trinaphthylene molecule.

Key words

Molecular Electronics, Single Molecule Computing, Logical Operation, STM

1. Introduction

The new molecular electronic approach called QHC (standing for Quantum Hamiltonian Computing)¹ has been recently proposed and demonstrated experimentally in which the complex functionality of a Boolean logic gate is fully implemented inside a single molecule without integrating or mimicking standard electronic components like rectifiers, switches, transistors or even qubit-like chemical groups along the molecular structure². QHC is based on the phenomenon that the eigenstates of a well-designed quantum system can be shifted in energy relative to a reference energy to conform to a Boolean truth table by locally perturbing this quantum system, where the local perturbations serve as logical inputs². The advantage of this approach is that the logical output can be measured locally at any position on the quantum system where the shifted in energy quantum eigenstates have a large electronic probability density. In the absence of a planar technology to perform such measurements with a picometer precision³, a low temperature Scanning Tunneling Microscope (LT-UHV-STM) must be used first to map the electronic probability density of the molecular electronic states involved and then to perform tunneling spectroscopy. Applied to molecular electronic circuit design, the QHC approach offers the possibility to measure the logical output of a logic gate without passing a current through the complete molecular structure of the circuit. This is an advantage with respect to other approaches trying to use a molecule per replicate of classical electronic components² in which by increasing the complexity of the intramolecular circuit the molecular system size would rapidly increase and consequently the tunneling intensity through the circuit would decay exponentially⁴.

A QHC molecule able to function like a NOR Boolean logic gate has been demonstrated experimentally using a single trinaphthylene molecule by authors^{5,6}. In these experiments, the tip of a LT-UHV-STM was used to manipulate and contact single Au atoms to each of the two input branches of the “Y” shaped trinaphthylene. Here, each Au atom functions as a classical digital input. This classical binary information (set by the interaction or absence of a single Au atom with the π system of the Y molecule) is converted into quantum information by trinaphthylene's electronic structure to perform the expected NOR digital logic operation. On a standard Slater

atomic orbitals basis set decomposition of the molecular orbitals impacted by those Au interactions, the amount of quantum information distributed along the molecule can be estimated theoretically by following how this decomposition is changing¹⁰ as compared to a free of Au atom input molecule. The logical output status of this gate is obtained by performing a local scanning tunneling spectroscopy (STS) measurement on the Y molecule's output branch to measure how the ground state of the trinaphthylene molecule is shifted in energy due to the Au atoms classical logical inputs relative to a Boolean truth table^{5,6}.

To prove the concept further, we have now studied how the π system size of a Y shaped molecule maintained the functioning of the NOR QHC logic gate by using a trianthracene molecule (anthra[2,3-*j*]heptaphene) (see Fig. 1) which is also a symmetric Y shaped molecule but it's longer since it has one phenyl more per branch. Single gold atoms were also manipulated with the STM tip to coordinate them at each of the 2 input branches of this Y molecule. The effects of each logical Au input on the low laying electronic states of this new Y molecule were measured by STM mapping the differential conductance in real space and also by recording dI/dV spectra at the end of the molecule's output branch. These dI/dV maps were recorded at voltages corresponding to the main electronic resonances of the trianthracene's tunneling spectra. In this article, we also discuss how the Y structure of the trianthracene molecule permits a moderation of the decay with length of the quantum information distribution when one Au atom is coordinated at one end of the trianthracene as compared to the initial trinaphthylene. In a trianthracene molecule, the Au atom electronic interaction can be detected at the other end of the transmission path, defined from the input to the output branch, showing no significant decay of the ground state shift induced by the coordination of one Au Atom in spite of the extended transmission path as compared to the shorter trinaphthylene. This has interesting implications for the future design of QHC logic gates more complex than a NOR gate.

2. Experiments

All experiments, molecule deposition, imaging, atom manipulation and electronic spectroscopy measurements, were carried out using a gold mono crystal with (111) surface plane orientation as

the substrate. Prior to deposition of the molecules and the extraction and manipulation of atoms, this mono crystal was cleaned via sputtering and annealing cycles. The trianthracene molecules were sublimed from a quartz crucible using evaporation parameters set to produce sub-monolayer molecular coverage on the Au(111) surface. After deposition, the Au(111) sample was pre-cooled using liquid helium and transferred to the low temperature STM chamber where a base pressure below 10^{-10} mbar and a cryogenic working temperature of ~ 7 K are normally maintained. Tunneling spectra and differential conductance maps were recorded using a standard lock-in spectroscopy method.

3. Results and discussion

LT-UHV-STM constant current images recorded after adsorption of the trianthracene molecules on Au(111) show that some molecules adsorbed at step edges while others are isolated on the Au(111) surface terraces. Imaged by the LT-UHV-STM, an isolated molecule reveals its Y shape with equal length branches. As presented in the image series in the Fig. 1, different sub-molecular features are observed upon varying the imaging bias voltage. To identify those features, two non-averaged dI/dV tunneling spectra recorded on a single trianthracene molecule are presented in Fig. 2a. For the dI/dV spectrum recorded at the end of the Y output branch two resonances can be clearly identified at -1.06 V and -1.33 V bias voltages, respectively. For the dI/dV spectrum recorded exactly at the phenyl node in between the 2 input branches, two other resonances can be identified at +1.63 V and +2.2 V bias voltages. These two resonances can also be observed by positioning the tip apex at the Y output branch end. In Fig. 2a, the separation between the first negative and the first positive resonances is about 2.69 V and corresponds to the energy separation between the ground and the first reduced states of the trianthracene molecule on Au(111). By comparison, this energy separation was 3.4 eV for the shorter trinaphthylene homologue deposited on Au(111)^{5,6}.

To identify the main molecular orbital (MO) contributions to those 4 low lying electronic resonances, constant current differential conductance dI/dV maps were recorded to measure the detailed spatial distribution of the Y molecule electronic eigenmode as presented in Fig. 2b. This

mapping is also essential to determine where to position the single Au atom at the end of the Y input branches, to set the logical inputs and the tip apex at the output branch end with respect to molecular skeleton, and to enhance the signal-to-noise ratio during the measurement of the logical output of the molecule logic gate. The identification of trianthracene's electronic resonances and their localization relative to the trianthracene structure had been performed experimentally by Guillermet *et al.*⁷ by comparing LT-UHV-STM and LT-UHV-NC-AFM images of trianthracene molecules physisorbed on a NaCl/Cu(111) surface. On such a surface, planar conjugated molecules are known to be very well decoupled electronically from the underlying metallic surface. This electronic decoupling in conjunction with cross-examination of experimental imaging and STM image calculations permitted an unambiguous identification of the main molecular orbital contributions to at least the first negative and positive electronic resonances of such molecule in a STM tunnel junction.

For an isolated trianthracene molecule adsorbed on Au(111), the Fig. 2b dI/dV maps recorded at -1.06 V and +1.63 volts are similar to the ones recorded for trianthracene on NaCl/Cu(111), corresponding to the molecule's first negative and positive resonances, already confirming that the trianthracene molecules on Au(111) are physisorbed. According to Elastic Scattering Quantum Chemistry (ESQC) dI/dV STM image calculations⁷, these dI/dV maps at -1.06 V and 1.63 V correspond to electronic resonances whose main MO contributors captured by the STM are the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) molecular orbitals of the trianthracene molecule, respectively. This reflects the fact that when physisorbed on Au(111) and in standard quantum chemistry, the HOMO and LUMO can be used to describe the virtual first oxidized and first reduced forms of the trianthracene molecule giving rise to the -1.06 V and +1.63 V tunneling electronic resonances. Following this interpretation, the two other resonances at -1.33 V and +2.2 V can be attributed in first approximation to the HOMO-1 and LUMO+1 MOs as also confirmed by ESQC calculations⁷. The HOMO dI/dV map in Fig. 2b clearly indicates the location of the tunnel junction conductance maxima, which is where the Au atoms should be positioned in order to ensure the maximum electronic interaction with the Y input branches. The cross examination between dI/dV maps and the corresponding trianthracene NC-AFM images reported by Guillermet *et al.*⁷ enables the identification of the spatial relationship between differential conductance lobes

captured in the dI/dV maps relative to the molecule's structure, hence facilitating the identification of the exact site for the gold-aromatic ring coordination that takes place after the manipulated atom is brought into interaction with the selected input branch, as well as the optimum location for the STM tip apex that records the dI/dV spectra and characterizes the logical output.

To set the logical inputs in a trianthracene molecule, Au atoms were produced by gently indenting the STM tip apex into the Au(111) surface⁸. Following this procedure, single Au atoms can be found around the indented area. Some of them were manipulated by STM so as to interact with an isolated trianthracene molecule and act as the logical inputs. In keeping with the previously established logical inputs on trinaphthylene⁵, a "1" logical input is performed on trianthracene when a single Au atom is manipulated towards one of its two input branches and coordinated to the corresponding terminal aromatic ring. An electronic re-organization of the trianthracene electronic structure results from such electronic interaction producing a shift in energy of trianthracene's ground state (imaged like its main HOMO contribution to the tunnel junction conductance). Aside from the (0,0) logical input configuration for a non-coordinated Y molecule, the three other (0,1), (1,0) and (1,1) logical input configurations were constructed by coordinating an Au atom each to one or two of the input branches. The corresponding configuration and STM constant current images are presented in Fig. 3. It is also possible to coordinate single Au atoms to any of the two aromatic rings located between the center of the molecule and the end of each branch. However, such Au-trianthracene complexes are very unstable and prone to movement during imaging or while recording the dI/dV spectra. This arises from the fact that an Au atom coordinated to the terminal aryl group of a branch induces a local deformation of this aromatic ring – the atom coordinates between two carbon atoms whose two corresponding terminal hydrogen atoms are pointing upwards with respect to the plane of the substrate^{5,9}. An aryl group within a Y branch is less deformable resulting in a rather unstable coordination. Such intermediate complexes were not considered further in this investigation.

In Fig. 3, topography STM images clearly indicate the position of the Au atoms coordinated at the end of the trianthracene input branches. As expected, significant changes are clearly visible in the internal contrast of the dI/dV maps from those of bare trianthracene on account of Au-

trianthracene electronic interactions, as shown in Fig. 3. A higher differential conductance is observed at the end of the Y output branch corresponding to the logical inputs configuration (0,1) and (1,1).

As presented in Fig. 4, the three dI/dV spectra recorded for bare trianthracene and its metal-molecule conformations corresponding (0,0), (0,1) and (1,1) were recorded by positioning the STM tip apex at one of the conductance maxima at the end of the Y output branch (observed in the dI/dV maps shown in Fig. 3). In the -2.0 V to +2.0 V potential range, it is always possible to capture the four electronic resonances of the Au-trianthracene complexes, as already observed in Fig. 2 for the bare trianthracene. To track better the trianthracene's QHC logic gate functioning, we decided to focus only on the negative voltage resonances because they are very sharp and easily distinguished from each other, while the resonances at positive voltages are much broader. At those negative voltages, the two native electronic resonances of the bare trianthracene molecule were better resolved (Fig. 4) as compared to those in the spectra in Fig. 2. After one Au input, the first -1.172 V resonance for the (0,1) or (1,0) logical input configuration is shifted down by -99 mV with respect to the bare trianthracene -1.073 V resonance. When a second Au atom is coordinated to trianthracene setting the (1,1) logical input, the first -1.138 V resonance is also shifted down relative to bare trianthracene's -1.073 V resonance, but only by 65 mV.

According to QHC theory, the logical output status of a QHC logic gate can be obtained by a spectral or a current intensity measurement at the output branch^{5,6}. With a physisorbed molecule and with the tip apex kept at large distance from the surface, the dI/dV measurements used are characteristic of a spectral output. To identify the molecular logic gate output status, the HOMO like resonance centered at -1.073 V was used as a reference for the logical output "1". Any input configuration giving rise to a resonance at the same voltage value also corresponds to "1" and resonances shifted by a voltage offset with respect to this reference or the absence of a resonance corresponds to a "0" logical output. Accordingly, the trianthracene molecule functions like a NOR gate but with a narrower margin for the different output resonances than for the shorter trinaphthylene molecule (See Fig. 5).

4. Conclusion

When a single Au atom is coordinated to one of the input branch of any of those Y molecules i.e. trianthracene or trinaphthylene, a shift in the molecules' ground state takes place as presented in Fig. 4 and Fig. 5. This shift was detected by recording the position in voltage (in energy relative to the Fermi energy) of the corresponding electronic resonances. For a conjugated molecule, this change in the electronic spectrum is distributed all along the molecule skeleton and is better detected at a conductance maximum as indicated by the Fig. 3 dI/dV maps. Interestingly and reported in Fig. 4, the effects of the electronic interaction between the Au atom and the terminal aromatic ring of one input branch can be detected rather far away in distance from the Au-molecule coordination site, actually at the other end of the molecule at the last phenyl ring of the output branch. As indicated by the QHC theory, there is a quantum information conversion from the classical input event, through the manipulation of the Au atom that is in contact with the input aromatic ring, and the resulting change in the π electronic structures of the molecule. Then, the information about the event of an Au atom interacting with a terminal phenyl group is distributed over the electronic states of the molecule. The number of π electronic states involved can be evaluated in detail by considering the change in the composition of the low laying in energy π electronic states decomposed on a standard Slater's orbital basis set¹⁰.

For a linear system like a long oligo-acene molecule, the orbital weight distribution of the perturbation induced by a classical logic input at one end of the molecule will decay very fast along the molecular skeleton and with the length of the molecule. Almost no ground state shift will be detectable at the opposite end of an oligo-acene of at least 10 linearly fused phenyl rings. For the trianthracene and trinaphthylene molecules, a comparison between their respective (0,0) to (0,1) resonance shift indicates only a small change, ΔV : 99 mV for trianthracene (Fig. 4) and ΔV : 94 mV for trinaphthylene (Fig. 5). Intuitively, an exponential decay is expected since the transmission path for trianthracene is longer by two phenyl as compared to trinaphthylene's. Indeed this phenomenon can be found from calculations using a simple linear tight binding (TB) model with alternant couplings along the TB chain. However the transmission of quantum information for a Y shape TB model featuring the alternant electronic coupling organization

through the whole Y topology is different. In this case, the decay of the shift resulting from an increase of the transmission path length is very slow because of the central node which plays the role of a “stub” as in a standard microwave circuit. This is a very interesting effect to consider in the design of more complex QHC logic gate molecules whose lateral spatial extension will be necessary, even if in QHC this extension would be very moderate¹ as compared to a standard molecular electronic intramolecular circuit design proposal¹¹. Further investigations with larger molecules are still necessary to confirm the moderate shift decay of the Y topology experimentally.

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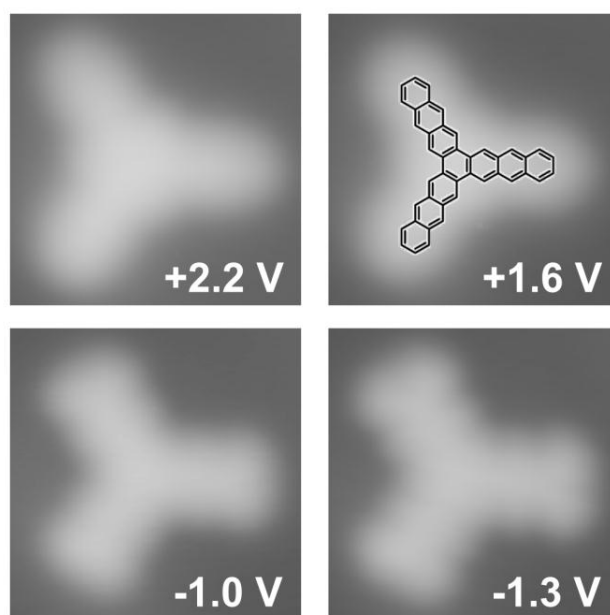


Fig. 1. LT-UHV-STM constant current topographic images of a ‘Y’ shape trianthracene molecule physisorbed on a Au(111) terrace taken at different bias voltages. Some intramolecular features are clearly seen at -1.3 V. The trianthracene molecular structure is represented on scale with the STM images recorded at +1.6 V. (image size: 2.5 x 2.5 nm).

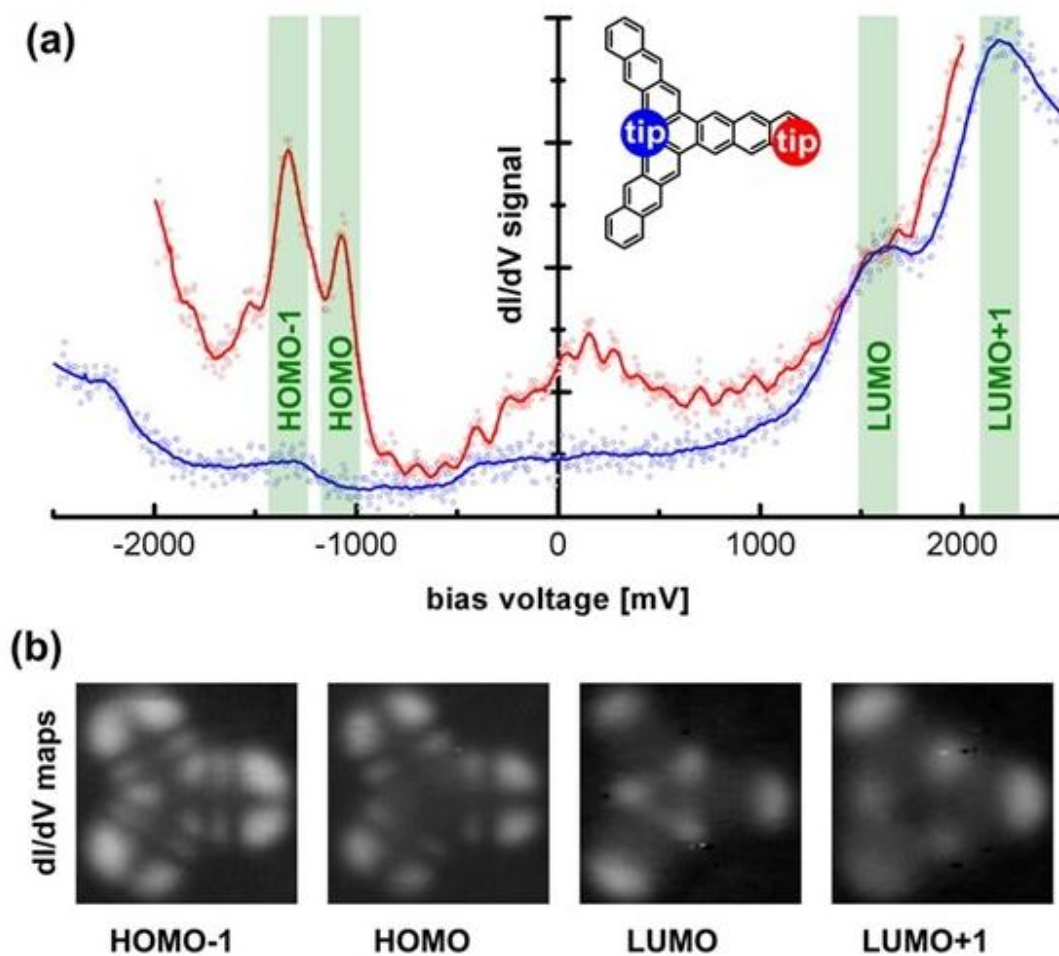


Fig. 2. (a) LT-UHV-STM dI/dV electronic tunneling spectra recorded at the two indicated locations on a single Y trianthracene molecule and (b) the corresponding constant current dI/dV maps recorded exactly at the 4 tunneling resonance maxima determined in (a): -1.33 V for HOMO-1, -1.06 for HOMO, +1.63 for LUMO and +2.2 V for LUMO+1. (image size: 2.5 x 2.5 nm).

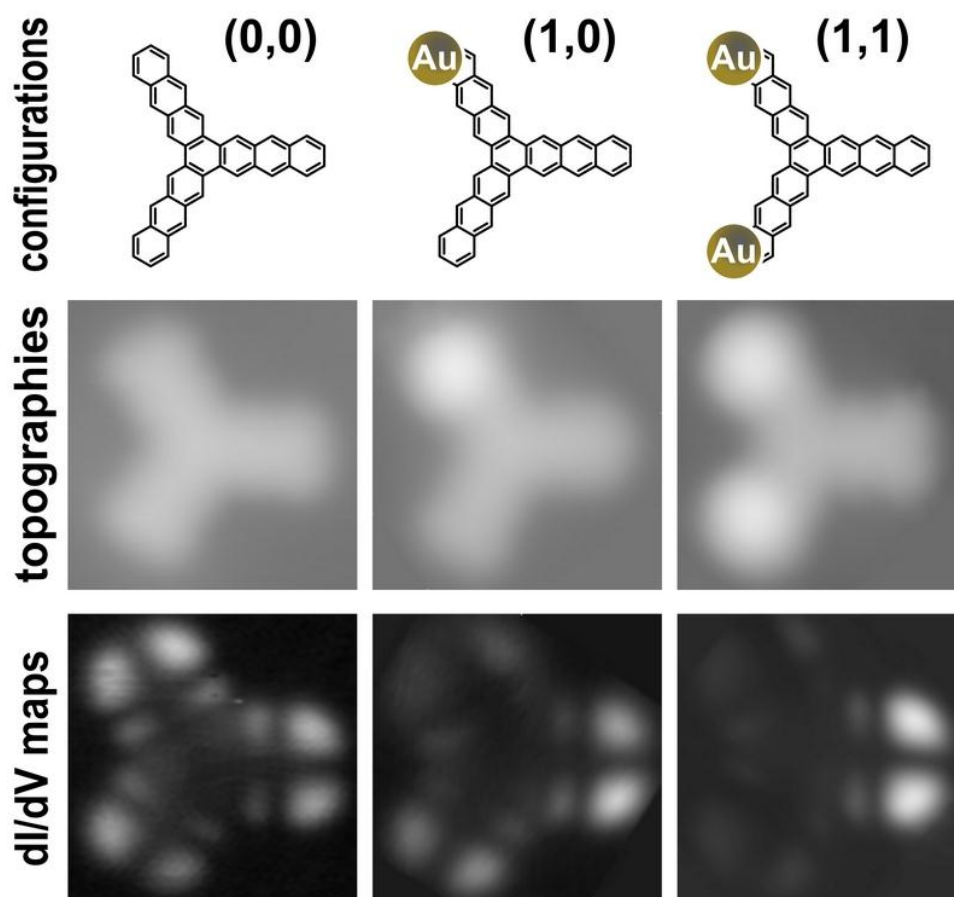


Fig. 3. Topographic images and dI/dV maps of all Au-trianthracene input conformations investigated. Each input conformation is indicated in parenthesis where, for example, (1,1) indicates that one atom was input at the position α and another one at β as indicated on the molecule models by solid circles representing the Au atoms (STM image size: 2.5 x 2.5 nm).

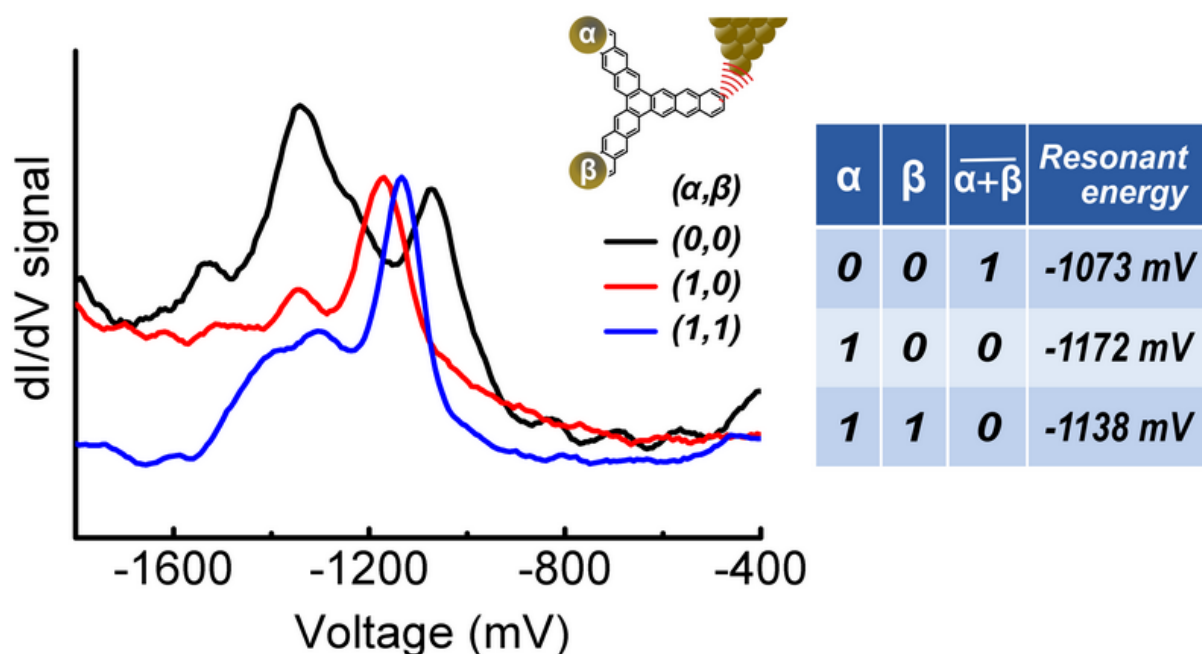


Fig. 4. dI/dV spectra of the constructed Au-trianthracene complexes corresponding to all (α, β) input conformations. The spectra were taken by positioning the STM tip over the output branch as shown in the sketch. Trianthracene's resonance centered at -1073 mV corresponding to the molecule's HOMO and the output i.e. 1, produced by the (0,0) input is selected as the molecule QHC energy reference. Accordingly, spectral shifts for the other inputs are also tabulated in a Boolean truth table showing that the molecule's output conforms with a NOR logic gate output.

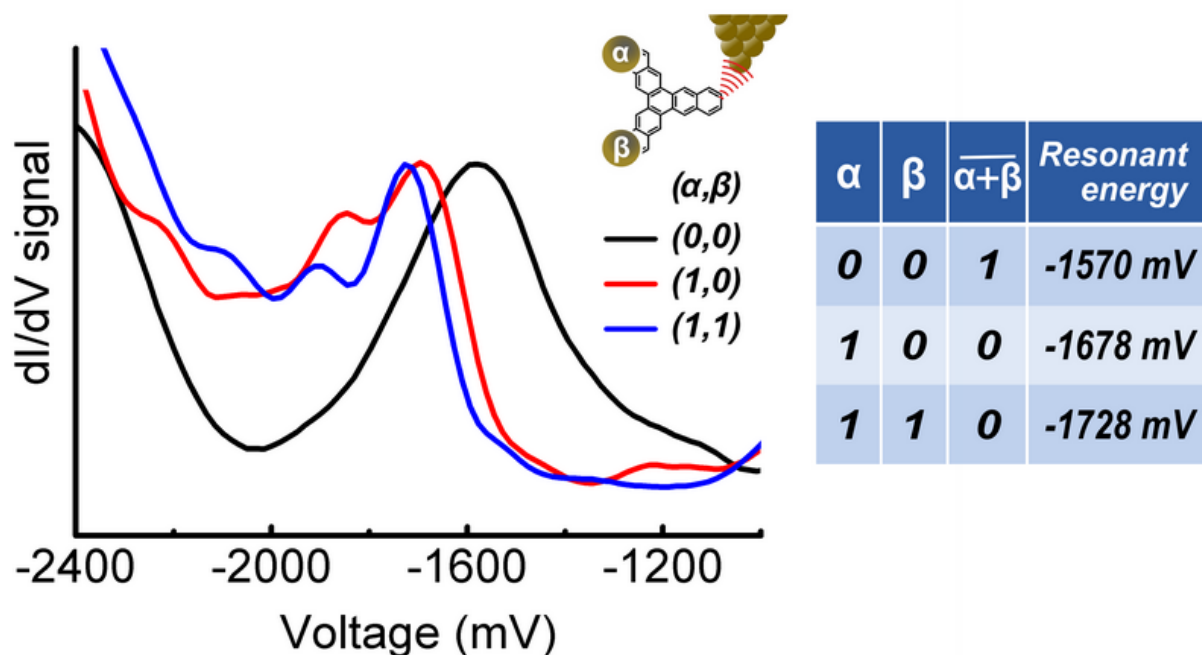


Fig. 5. For comparison, the dI/dV spectra of the constructed Au-trinaphthylene complexes corresponding to all (α, β) input conformations. The spectra were taken by positioning the STM tip over the output branch as shown in the sketch. The short trinaphthylene's resonance centered at -1570 mV corresponding to the molecule's HOMO and to the logical output "1" of the (0,0) input configuration is selected as the molecule QHC reference. Accordingly spectral shifts for the other inputs are also tabulated in a Boolean truth table showing that the molecule's output conforms with a NOR logic gate output.

Graphical abstract

